

(19) Japan Patent Office (JP)

(12) KOKAI TOKKYO KOHO (A)

(11) Unexamined patent application publication number (Kokai) Heisei

5-202182

(43) Publication date: Heisei 5 (1993) August 10

(51) Int. Cl.5	ID No.	Office File No.	FI Technical points
C 08 G 64/08	NQA	8933-4J	
B 29 C 45/00		7344-47	
C 08 L 83/10	LRR	8319-4J	
// B 29 K 69:00			

Examination: Not yet applied for Claims: 7 (Total 7 pages)

(21) Patent application number: Heisei 4-11161

(22) Application date: Heisei 4 (1992) January 24

(71) Applicant 000004466

Mitsubishi Gas Chem Co Inc

5-2 banchi, 2-Chome, Marunouchi, Chiyoda-ku, Tokyo

(72) Inventor Ogawa Noriyoshi

Mitsubishi Gas Chem Co Inc, Osaka plant

12-banchi, 2-chome, Kamishima-cho, Toyonaka, Osaka

(72) Inventor Kanayama Satoshi

12-banchi, 2-chome, Kamishima-cho, Toyonaka, Osaka

Mitsubishi Gas Chem Co Inc, Osaka plant

(54) Title of the invention: Injection molding of polycarbonate copolymer

(57) Abstract

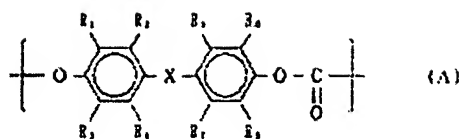
Purpose: To obtain injection moldings with improved surface characteristics (such as lubricating properties and abrasion resistance) while maintaining transparency and mechanical characteristics (such as flexural or tensile characteristics) of the polycarbonate.

Constitution: The objective polycarbonate copolymer injection moldings are injection moldings made from a polycarbonate-polysiloxane copolymer having a structural unit consisting of a dihydric phenol and a polysiloxane, where the percentage of the structural unit in the polysiloxane is 0.1-20 wt% and the concentration of the polysiloxane structural unit in a surface layer, whose depth from the molding surface is less than 50Å, is 2 or more times that of the polysiloxane structural unit in a core layer, whose depth is $\geq 50\text{\AA}$.

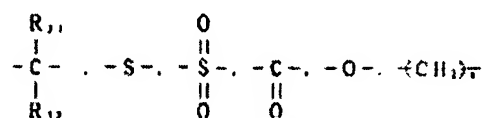
Claims

1. Polycarbonate copolymer injection moldings, having a structural unit given by the below-mentioned general formula (A) and formed by the injection molding of polycarbonate polysiloxane copolymer, where the percentage of the structural unit given by (B) is 0.1~20wt% and the concentration of the structural unit (B) in a surface layer, whose depth from the molding surface is less than 50Å, is two or more times that of the structural unit (B) in a core layer, whose depth is $\geq 50\text{\AA}$.

(Conversion 1)



(In the formula, $\text{R}^1 \sim \text{R}^8$, respectively stand for a suitable alkyl group or allyl group, which may have hydrogen, halogen or a substituent group, R^9 and R^{10} respectively stand for a suitable alkyl group or allyl group, which may have hydrogen, halogen or a substituent group, X is (Conversion 2)



Here, R^{11} and R^{12} respectively stand for either a suitable alkyl group or allyl group, which may have hydrogen, halogen or a substituent group, or it may stand for a group that forms a carbon ring or a complex ring by bonding together R^{11} and R^{12} , a indicates a positive number ≥ 1).

2. The molding mentioned in claim 1 has a thickness of 0.4~10.0 μm .
3. The molding mentioned in claim 1, the percentage of the structural unit (B) in polycarbonate polysiloxane copolymer, is 1~20wt% and the concentration of the structural unit (B) in a surface layer of depth less than 50., is 2~100wt%.
4. In the molding mentioned in claim 1, the viscosity average molecular weight of the polycarbonate polysiloxane copolymer is 15,000~50,000.
5. In the molding mentioned in claim 1, the structural unit (A), is a compound derived from dihydric phenol, which is selected from the group formed by

2,2-bis(4-hydroxyphenyl)propane and 1,1-bis(4-hydroxyphenyl)cyclohexane.

6. In the molding mentioned in claim 1, the structural unit (B), is
 α,ω -bis[3-(o-hydroxyphenyl)propyl]polymethylsiloxane.
7. In the molding mentioned in claim 1, the polycarbonate polysiloxane copolymer is a random copolymer.

Detailed description of the invention

[0001]

Industrial usage areas: This invention provides polycarbonate injection moldings with improved lubricating properties and abrasion resistance and in particular, concerns the injection moldings of polycarbonate siloxane, where the concentration of the siloxane structural unit in a surface layer, is higher than that in a core layer.

[0002]

Traditional technology: Generally, the improvement of surface characteristics, such as lubricating properties and abrasion resistance, involves addition of silicon oil or blending of polysiloxane. However, if less quantity is added, the improvement in surface characteristics is not adequate. On the other hand, if an excessive quantity is added, due to the poor compatibility with polycarbonate, it results in many defects such as white turbidity in the molding, decline in the mechanical characteristics (such as flexural or tensile characteristics) and moreover, due to abrasion and decidue, the surface characteristics cannot be maintained for a long-term usage.

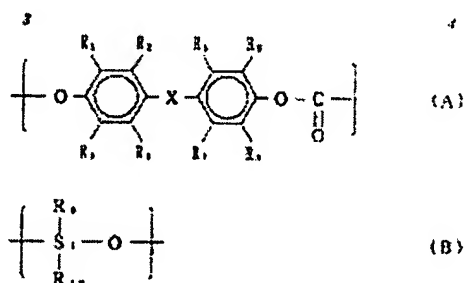
[0003]

Procedure for solving the problem: This invention provides solution for following problems.

For example, this invention concerns the polycarbonate copolymer injection moldings, having a structural unit given by the below mentioned general formula (A) and formed by the injection molding of polycarbonate polysiloxane copolymer, where the percentage of the structural unit given by (B) is 0.1~20wt% and the concentration of the structural unit (B) in a surface layer, whose depth from the molding surface is less than 50 Å., is two or more times that of the structural unit (B) in a core layer, whose depth is $\geq 50\text{Å}$.

[0004]

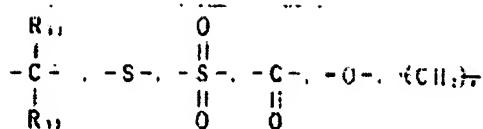
Conversion 3



[0005] (In the formula, $\text{R}^1 \sim \text{R}^8$, respectively stand for a suitable alkyl group or allyl group, which may have hydrogen, halogen or a substituent group, R^9 and R^{10} respectively stand for a suitable alkyl group or allyl group, which may have hydrogen, halogen or a substituent group, X is

[0006]

[Conversion 4]

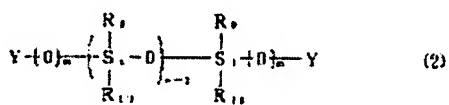
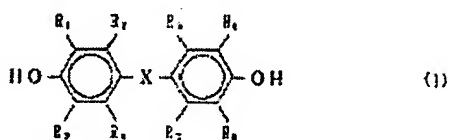


[0007] Here, R^{11} and R^{12} respectively indicate either a suitable alkyl group or allyl group, which may have hydrogen, halogen or a substituent group, or it may indicate a group that forms a carbon ring or a complex ring by bonding together R^{11} and R^{12} , a indicates a positive number ≥ 1). The desired percentage of the structural unit given by (B) is 1~20wt% and the structural units (A) and (B) should repeat randomly.

[0008] We shall now explain about the constitution of this invention. The polycarbonate resin used in this invention is a polycarbonate polysiloxane copolymer, obtained by the copolymerization of a dihydric phenol given by the below mentioned general formula (1) and polysiloxane given by the general formula (2)

[0009]

Conversion 5



[0010] (In the general formula (1), X , $R^1 \sim R^8$, are same as in general formula (A), n is an integer between 1 and 1000. In the general formula (2), R^9 and R^{10} , respectively stand for a suitable alkyl group or allyl group, which may have hydrogen, halogen or a substituent,

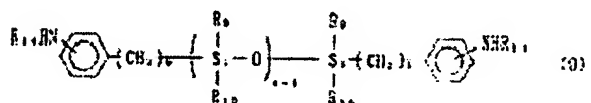
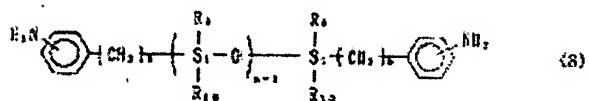
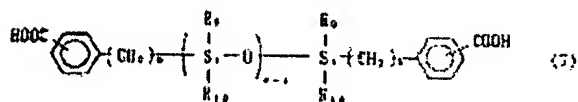
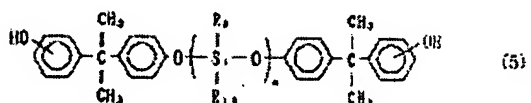
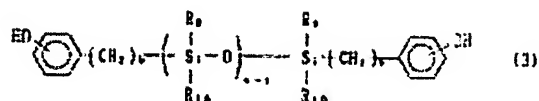
Y stands for halogen, $-R^{13}OH$, $-R^{13}COOH$, $-R^{13}NH_2$, $-R^{13}NH_2$, $-SH$, R^{13} represents a straight chain, branched chain, or a cyclic alkylidene group, allyl substituent alkylidene group, allyl group, R^{14} stands for an alkyl, alkenyl, allyl, aralkyl group and m indicates either 0 or 1.), with phosgene, carbon ester or chloroformate, where the percentage of the structural unit given by the general formula (B) is 0.1~20wt%. If the percentage of the structural unit given by the general formula (B) exceeds 20wt%, the transparency declines. The percentage of the structural unit given by (B) is desirably $\geq 1.0\text{wt}\%$ and if it is lesser than 1.0wt%, sufficient concentration of polysiloxane would not be obtained on the surface and the surface characteristics would deteriorate. The viscosity average molecular weight of the copolymer should be 15,000~50,000. If the viscosity average molecular weight is lesser than 15,000, the molding will not have enough hardness and if it exceeds 50,000, the productivity will decline.

[0011] Further, the examples for dihydric phenol, given by the general formula (1), which is used as a raw material for co-polycarbonate resin in this invention, include bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)ketone, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane(bisphenol A;BPA), 2,2-bis(4-hydroxyphenyl)butane, 1,1-bis(4-hydroxyphenyl)cyclohexane(bisphenol Z; BPZ), 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 2,2-bis(4-hydroxy-3-chlorophenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, bis(4-hydroxyphenyl)diphenylmethane, etc. Among these, 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)cyclohexane, are particularly preferable.

[0012] The examples of polysiloxane, mentioned in the earlier general formula (2), include

[0013]

Conversion 6



[0014] (In the earlier mentioned general formula (3)~(9), same as formula (1), R^9 and R^{10} , respectively stand for a suitable alkyl group or allyl group, which may have hydrogen, halogen or a substituent, R^{14} indicates alkyl, alkenyl, allyl, aralkyl, similar to Y of general formula (2), and n is an integer between 1 and 1000, b is a positive integer.), etc. Among these, α,ω -bis[3-(o-hydroxyphenyl)propyl]polydimethylsiloxane is particularly desirable.

[0015] The dihydric phenol, indicated by the earlier mentioned general formula (2), can be easily prepared by carrying out hydrosilylation reaction for a phenol having olefin type unsaturated carbon-carbon bond, ideally, vinylphenol, arylphenol, isopropylphenol, at the end of the polysiloxane chain having a fixed degree of polymerisation, n.

[0016] An end terminating agent or a molecular weight modifier is generally used for the preparation of polycarbonate resins. Compounds that have monohydric phenolic hydroxyl group, such as long chain alkylphenol, aliphatic carboxylic acid chloride, aliphatic carboxylic acid, hydroxy alkyl benzoate, hydroxyphenyl alkyl acidic ester, alkylether phenyl, etc., are used as end terminating agent, besides the usual phenol, p-tertiarybutylphenyl, tribromophenol, etc. Their usage amount is 100~0.5 moles per 100 moles of the entire dihydric phenolic compound used, the most desired range being 50~2 moles and it is also possible to use two or more compounds at the same time. Further, 0.01~3mole%, particularly between the range of 0.1~1.0mole%, of a ramification agent can also be jointly used, with respect to the above mentioned dihydric phenolic compound, to result in branched polycarbonate. The examples of ramification agents include, polyhydroxy compounds and 3,3-bis(4-hydroxyallyl)oxiindole(=isatin bisphenol), 5-chloroisatin, 5,7-dichloroisatin, 5-bromeisatin, etc., illustrated by floroglycine, 2,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-2, 1,3,5-tri(2-hydroxyphenyl)benzol, 1,1,1-tri(4-hydroxyphenyl)ethane, 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol, $\alpha,\alpha'\alpha''$ -tri(4-hydroxyphenyl)-1,3,5-triisopropylbenzene, etc.

[0017] If required, various types of common additives could be compounded with the polycarbonate resin used in this invention, and these include, reinforcing agent, filler, stabilizer, ultraviolet radiation absorbent, antistatic agent, lubricant, mold lubricant, dye, pigment and other flame retarders or elastomers used for improving impact resistance.

[0018] The injection moldings mentioned in this invention are formed by the usual injection molding method. While releasing polysiloxane copolymer, polysiloxane is shifted to the surface by the injection molding method that involves shearing, and siloxane is concentrated at the ends. The desired shearing speed is $5 \times 10^3 \sim 5 \times 10^6$ (to the power 6) (1/sec). If it is lesser than 5×10^3 , the siloxane concentration would be insufficient and if it exceeds 5×10^6 (to the power 6), the necessary flowability would not be obtained and injecting would become difficult. From the viewpoint of thermal resistance and flowability, the desired resin temperature is 250~340°C.

[0019] The thickness of injection moldings should generally be 0.4~10.0μm. If the thickness falls below 0.4μm, the molding would lack the desired hardness and if it exceeds 10μm, the moldability would become poor. In the injection moldings mentioned in this invention, the concentration of the structural unit (B) in a surface layer, whose depth from the molding surface is less than 50Å, is two or more times that of the structural unit (B) in a core layer, whose depth is $\geq 50\text{Å}$. and if the percentage of the structural unit (B) is 1~20wt%, the concentration of the structural unit (B) in the surface layer should be in the range of 2~100wt%.

[0020] The composition analysis of the polycarbonate polysiloxane copolymer injection moldings, mentioned in this invention, having a surface thickness of less than 50Å, is done by determining C-1S, O-1S, Si-2P, by using ESCALAB, made by V.G. Scientific company. As for C (carbon), the detection was done for Shake up satellite peak that originates in $\pi-\pi^*$ in C-C, C=C, C-II, C-Si original peak, C-O original peak of 286.1~286.2eV, carbonate bond (OCOO) original peak of 290.5~290.7eV, unsaturated bond of 291.7~292.3eV. As for O (oxygen), the detection was done for C=O, Si-O

original peak of 532.2~532.3eV, C-O original peak of 533.9~534.0eV. As for Silicon, the detection was done for $\text{-O-Si(CH}_3\text{)}_2\text{-O}$ (siloxane) original peak of 102eV. Although the measurement depth of ESCA varies depending upon the atomic and electronic energy, the average free process for C, O, Si at 100~600eV is $\leq 20\text{\AA}$ and in most cases, the detection of atoms at a depth of $\geq 50\text{\AA}$, is not done. As a result, ESCA is used to measure siloxane concentration of $\leq 50\text{\AA}$ surface layer depth. The analysis of a core layer having surface layer depth of $\geq 50\text{\AA}$, is done by doing Argon etching on the surface, then measuring the cut segment of 50\AA and then comparing it.

[0021]

Examples

Example 1

91.2 kg of bisphenol A (BPA) and 5.95 kg (set the structural formula (B), so that it becomes 5 wt%) of dihydric phenol, given by the general formula (3) (where, R^9 and R^{10} are respectively methyl group, ortho bonded by $n=41$, $b=3$), are added to 580 litres of 8.8% (W/V) sodium hydroxide aqueous solution, then 100gms. of hydrosulfite is added and melted. To this, 360 litres of methylene chloride was added and it was stirred while maintaining it at a temperature of 15°C , 1.44kg of p-t-butylphenol (PTBP) was added and then 53.1kg of phosgene was blown-in in a time period of 60 minutes. After completion of the blowing, the solution was vigorously stirred, the reaction fluid was emulsified and after emulsification, 100ml. of triethylamine was added and it was polymerised by stirring for approximately 1 hour. The polymer solution was separated into water layer and organic layer and after neutralizing the organic layer with phosphoric acid, it was repeatedly washed with water till the pH of the washing solution became neutral, 470litres of isopropanol was then added and the polymer was precipitated. After filtering the precipitate, polycarbonate polysiloxane copolymer (PC-Si) resin, in the form of

white-colored powder, was obtained after drying. From the obtained PC-Si resin, injection moldings having height 127mm, width 12.7mm and thickness 3.2mm were prepared by the injection molding machine made by MEIKI, under conditions, such as nozzle diameter 3mm, resin temperature 300°C, screw frequency 50 r.p.m (screw dia. 45mm) and injection speed 1.6cm/sec. The shearing speed at this point was 9.8×10^3 (1/sec), with injection rate being 26cc/sec. The shearing speed was obtained by the following formula:

$$\omega.a \text{ (shearing speed)} = 4Q/\pi R^3$$

Q = Bulk flow rate being passed out of the capillary (cm³)

R = capillary radius (cm)

Each of the following tests was conducted on the obtained injection moldings and the results are shown in table 1.

[0022] The concentration (wt%) of siloxane in a surface layer, whose depth from the surface of the injection molding is lesser than 50Å and the concentration (wt%) of siloxane in a core layer, with depth $\geq 50\text{Å}$, was determined (C-1S, O-1S, Si-2P) by using the earlier mentioned ESCA. Further, the random characteristics of the moldings were recorded in table 1, by examining the existence of non-uniformity in the fibrous state, through TEM observation and its presence was indicated by a ×, whereas, absence was indicated by a ○. The abrasive nature of the moldings was determined by measuring the abrasion amount mg by Taber abrasion test (load 1kg, CS-17 ring, toluene atmosphere, 24 hrs).

[0023] Example 2

Same as in example 1, except for using 107.2kg of bisphenol Z (BPZ), instead of BPA.

The result is shown in table 1.

[0024] Example 3

Same as in example 1, except for changing the concentration of the structural formula (B), obtained from dihydric phenol (R^9 and R^{10} are respectively methyl group, ortho bonded by $n=41$, $b=3$,) given by the earlier mentioned general formula (3), to 1wt%. The result is shown in table 1.

[0025] Example 4

Same as in example 1, except for changing the concentration of the structural formula (B), obtained from dihydric phenol (R^9 and R^{10} are respectively methyl group, ortho bonded by $n=41$, $b=3$) given by the earlier mentioned general formula (3), to 20wt%. The result is shown in table 1.

[0026] Example 5

Same as in example 1, except that in the dihydric phenol given by the general formula (3), R^9 and R^{10} are respectively methyl group, para-bonded by $n=41$, $b=2$. The result is shown in table 1.

[0027] Example 6

Same as in example 1, except that in the dihydric phenol given by the general formula (3), R^9 and R^{10} are respectively methyl group, ortho-bonded by $n=101$, $b=3$. The result is shown in table 1.

[0028] Example 7

Same as in example 1, except that in the dihydric phenol given by the general formula (3), R^9 is methyl group and R^{10} is phenyl group, ortho-bonded by $n=41$, $b=3$. The result is

shown in table 1.

[0029] Example 8

The dihydric phenol mentioned here is that which is given by the general formula (4), R^9 and R^{10} are respectively methyl group, $n=41$ and besides this, it is same as in example 1.

The result is shown in table 1.

[0030] Comparative example 1

Same as example 1, except that the dihydric phenol, including siloxane, was not used at all. The result is shown in table 1.

[0031] Comparative example 2

Same as example 2, except that the dihydric phenol, including siloxane, was not used at all. The result is shown in table 1.

[0032] Comparative example 3

Same as example 1, except that the dihydric phenol given by the general formula (3), where R^9 and R^{10} are respectively methyl group, ortho bonded by $n=41$, $b=3$, is used in a way that the structural unit (B) in the copolymer, becomes 0.9wt%. The result is shown in table 1.

[0033] Comparative example 4

Same as example 1, except that the dihydric phenol given by the general formula (3), where R^9 and R^{10} are respectively methyl group, ortho bonded by $n=41$, $b=3$, is used in a way that the structural unit (B) in the copolymer, becomes 25wt%. The result is shown in table 1.

[0034] Comparative example 5

The dihydric phenol given by the general formula (3), where R^9 and R^{10} are respectively methyl group, ortho bonded by $n=41$, $b=3$, is blended in the polycarbonate mentioned in example 1, so that the percentage of the structural formula (B) becomes 5wt%. The result is shown in table 1.

[0035]

Table 1

Wt% of the phenol*1 given by formula (B)	<u>Monomer</u>		Viscosity average <u>molecular weight</u>	<u>Film characteristics</u>		Random <u>features</u> Hardness of lead <u>pencil</u>	<u>Abrasion</u> <u>resistance</u> Abrasion <u>amount</u>	
	wt% of the siloxane*2 given by formula (A)			Conc. of siloxane in surface layer with depth <50 Å(wt%)				
Eg.1	BPA 95.0	① 5.0	3.0×10^4	14	○	2H	13	
Eg.2	BPZ 95.0	① 5.0	3.0×10^4	15	○	2H	13	
Eg.3	BPA 99.0	① 1.0	3.0×10^4	5	○	H	18	
Eg.4	BPA 80.0	① 20.0	3.2×10^4	43	○	3H	10	
Eg.5	BPA 95.0	② 5.0	3.0×10^4	12	○	2H	14	
Eg.6	BPA 95.0	③ 5.0	3.0×10^4	15	○	2H	15	
Eg.7	BPA 95.0	④ 5.0	3.3×10^4	12	○	2H	17	
Eg.8	BPA 95.0	⑤ 5.0	3.0×10^4	16	○	2H	14	
Co.Eg.1	BPA 100.0	- 0.0	3.0×10^4	-	○	HB	32	
Co.Eg.2	BPZ 100.0	- 0.0	3.2×10^4	-	○	H	23	
Co.Eg.3	BPA 99.91	① 0.09	3.0×10^4	0.5	○	H	26	
Co.Eg.4	BPA 75.0	① 25.0	3.4×10^4	56	×	3H	10	
Co.Eg.5	BPA 95.0	①*3 25.0	3.0×10^4	9	×	H	25	

*1 BPA: bisphenol A, BPZ: bisphenol Z

*2① : polysiloxane, given by the general formula (3), where R^9 and R^{10} are respectively methyl group, ortho bonded by $n=41$, $b=3$

② : polysiloxane, given by the general formula (3), where R^9 and R^{10} are respectively methyl group, para bonded by $n=41$, $b=2$

③ : polysiloxane, given by the general formula (3), where R^9 and R^{10} are respectively methyl group, ortho bonded by $n=101$, $b=3$

④ : polysiloxane, given by the general formula (3), where R^9 is methyl group, R^{10} is phenyl group ortho bonded by $n=41$, $b=3$

⑤ siloxane, given by the general formula (4), where R^9 and R^{10} are respectively methyl group, $n=41$.

*3 After blending monomer①

[0036]

Results of the invention: In the injection moldings of polycarbonate polysiloxane copolymer, mentioned in this invention, the polysiloxane segments get collected selectively on the top surface (surface layer depth lesser than 50Å) and since this becomes 2 times or more than that of the core layer with depth $\geq 50\text{\AA}$, polycarbonate injection moldings, with better than expected surface characteristics (improvement of lubricating characteristics, abrasion resistance), can be achieved even with a small amount of polysiloxane. Further, if the injection moldings of polycarbonate polysiloxane copolymer, mentioned in this invention, are compared with the injection moldings of the compound formed by polycarbonate resin and polysiloxane, where polysiloxane has the same concentration, it is seen to have the additional advantages like, no white turbidity and improved transparency, and at the same time, the mechanical characteristics of the polycarbonate (such as flexural or tensile characteristics), can be maintained.

Procedure revision

Date of presentation: Heisei (4) January 30

Procedure revision 1

Document to be revised: Text of specifications

Point to be revised: Claim 2

Revision method: modification

Details of revision

Claim 2: The molding mentioned in claim 1 has a thickness of 0.4~10.0mm.

Procedure revision 2

Document to be revised: Text of specifications

Point to be revised: 0019

Revision method: modification

Details of revision

[0019] The thickness of injection moldings should generally be 0.4~10.0mm. If the thickness falls below 0.4mm, the molding would lack the required hardness and if it

exceeds 10mm, the moldability would become poor. In the injection moldings mentioned in this invention, the concentration of the structural unit (B) in a surface layer, whose depth from the molding surface is less than 50 μ m, is two or more times that of the structural unit (B) in a core layer, whose depth is $\geq 50\mu$ m. and if the percentage of the structural unit (B) is 1~20wt%, the concentration of the structural unit (B) in the surface layer, should be in the range of 2~100wt%.